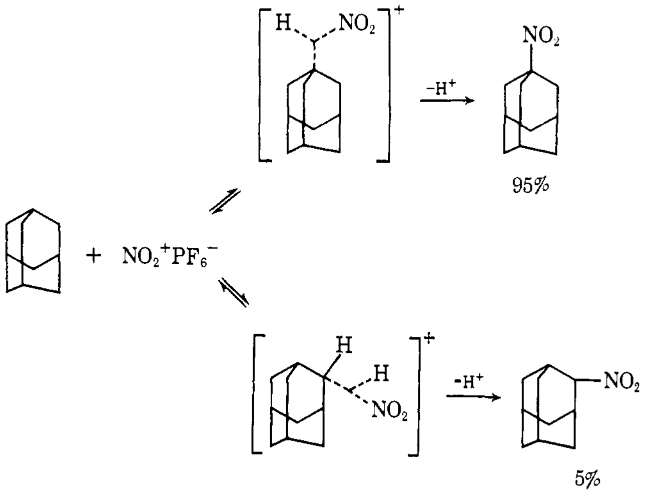
the cleaved alkylcarbenium ions) or secondary alkylation products, themselves capable of undergoing reaction with the nitronium salt.

Frontside attack by the electrophile, as suggested, should result in retention of optical activity, if reaction was carried out on an optically active hydrocarbon. Our studies in this regard are in progress and will be reported later. We have, however, already been able to carry out NO_2^+ nitration of rigid systems, like adamantane.

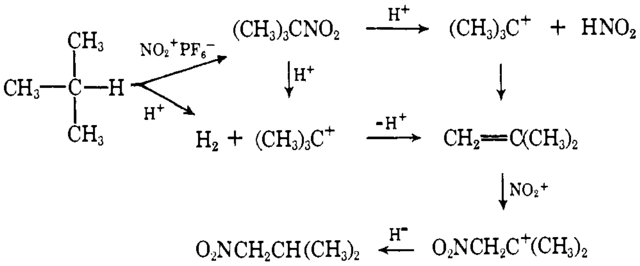
The ease and predominant formation of the tertiary bridgehead 1-nitroadamantane clearly indicates the suggested mechanism since no "backside" attack is possible through the cage compound.



Contrasted with electrophilic aromatic nitration, electrophilic aliphatic nitrations are much affected by protolytic denitrations, which particularly with tertiary and secondary nitro compounds are of major importance. The fact that denitration affects electrophilic aliphatic nitration can be best demonstrated in the case of 2-nitro-2-methylpropane which was found to undergo protolytic cleavage in FSO_3H-SbF_5, $HF-SbF_5$, and also in $HF-PF_5$ solution even at −80°. The protolytic cleavage reaction yields *tert*-butyl cation and nitrous acid (or subsequently, nitrosonium ion). No nitronium ion is formed, as indicated by absence of any aromatic nitration product found when *tert*-$C_4H_9NO_2$ was treated with benzene and toluene in the presence of strong acids; *i.e.*, only *tert*-butylated products were obtained.

$$(CH_3)_3CNO_2 \overset{H^+}{\rightleftharpoons} (CH_3)_3CNO_2H^+ \longrightarrow (CH_3)_3C^+ + HNO_2$$

Whereas our studies centered so far primarily on the feasibility of the nitration of alkanes (cycloalkanes) with nitronium salts in aprotic solvent systems, once reactions are demonstrated they can, of course, also be carried out under more conventional conditions. Mixed acid ($HNO_3-H_2SO_4$) nitration of isobutane at 50° gave the following nitroalkane composition: CH_3NO_2, 28%; $CH_3CH_2NO_2$, 4.9%; $(CH_3)_2CHNO_2$, 0.5%, $(CH_3)_3CNO_2$, 66.6%. Mixed acid nitration can be complicated by protolytic cleavage of product nitroalkanes, by isomerization of the hydrocarbon, oxidative side reactions, and, if higher reaction temperatures are applied, by free-radical nitration products. Nitroethane and 2-nitropropane formed in small amounts in the mixed acid nitration of isobutane can result from nitration of propane, formed *via* subsequent hydride transfer in the nitrolysis yielding nitromethane. In principle, however, there seems to be no reason why electrophilic aliphatic nitration should not become a general reaction, with a variety of nitrating agents capable to act as precursors to the nitronium ion. Anhydrous hydrogen fluoride and fluorosulfuric acid were found as improved solvents for the nitration of methane with nitronium salts. In these strong acid solvents even under the mild reaction conditions (room temperature) at least tenfold increased yields (~1%) could be obtained. As no protolytic reactions of methane take place in HF under the reaction conditions, side reactions are not observed. This is not the case in the nitration of isobutane in HF solution, where 90% of the nitroalkanes obtained consisted of 1-nitro-2-methylpropane. Since only traces of this isomer were found in nitronium salt nitration in aprotic CH_2Cl_2–sulfolane solution, the formation of 1-nitro-2-methylpropane must be considered due to formation of isobutylene (either from isobutane itself in HF containing PF_5 or more probably from the protolytic cleavage of 2-nitro-2-methylpropane).



The polar nitro group with its unshared electron pair donor oxygen atoms can act as a strong internal nucleophile and facilitates nitrous acid cleavage. If this effect is indeed of importance, it could also suggest that in the reverse step, *i.e.*, the NO_2^+ nitration of isobutane, the proton is removed internally by the oxygen atom of the polar nitro group.

The ease of protolysis of tertiary (and to a lesser degree secondary) aliphatic nitro compounds explains in part the complex reaction mixtures obtained in mixed acid nitrations of alkanes.

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Organometallic Chemistry. I. The Ethylene- and Norbornylenemercurinium Ions

Sir:

Mercurinium ions have been postulated as intermediates in the electrophilic addition of mercuric salts to olefins, in hydroxymercuration reactions, in oxidation reactions involving mercuric salts, and in certain Friedel–Crafts reactions.[1] Although there is extensive

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(1) For a recent review of the role of mercurinium ions in these reactions see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

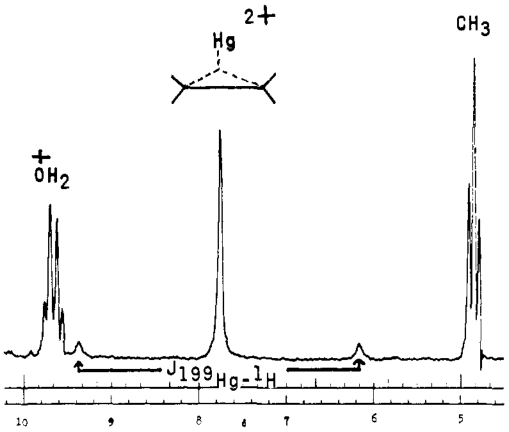


Figure 1. Pmr spectrum (60 MHz) of 2-methoxyethylmercuric chloride in FSO_3H-SbF_5-SO_2 at −30°.

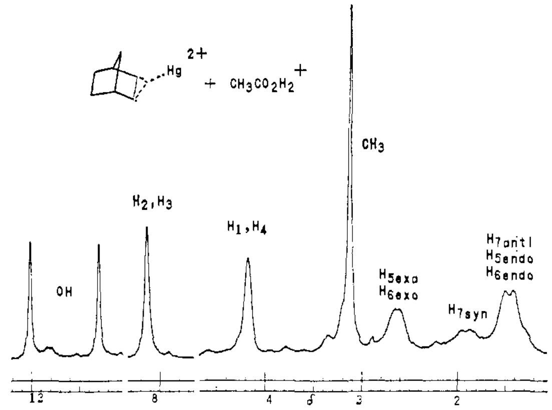


Figure 2. Pmr spectrum (100 MHz) of *exo-cis*-3-hydroxy-2-norbornylmercuric acetate in FSO_3H-SbF_5-SO_2 at −70°. (The acid and H_3O^+ peaks which appear between δ 10 and 12 were deleted for simplicity.)

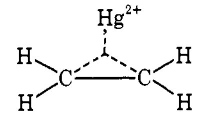
indirect evidence for the intermediacy of these ions, there has been no direct observation of a mercurinium ion.[2-5]

In a recent molecular orbital treatment of electrophilic additions of olefins[6] it was implied that under suitable experimental conditions mercurinium ions should be capable of independent existence. We now wish to report observation of the first stable, long-lived mercurinium ions.

When 2-methoxyethylmercuric chloride is added to a solution containing FSO_3H-SbF_5-SO_2 at −78° and the mixture is warmed to −10° with vigorous stirring for several minutes, the resulting clear solution (cooled back to −30°) exhibits a proton magnetic resonance (pmr) spectrum (Figure 1) consisting of a triplet (δ) (4.80), a singlet (7.68), and a quartet (9.77). The triplet and quartet are due to protonated methanol.[7] The singlet at δ 7.68 shows coupling to mercury, $J_{^{199}Hg-^1H}$ = 190 cps, and is assigned to the mercurinium ion.[2]

$$CH_3OCH_2CH_2HgCl \xrightarrow[SO_2]{FSO_3H-SbF_5}$$

$CH_3OH_2^+$ +



(1)

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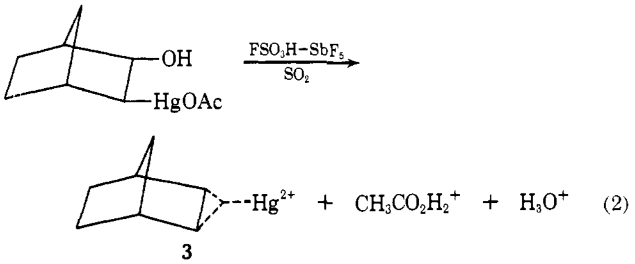
Ion **2** may also be obtained in SbF_5-SO_2, FSO_3H-SbF_5-SO_2ClF, and SbF_5-SO_2ClF solution and from 2-ethoxyethylmercuric chloride under each of the above conditions (with protonated ethanol as the by-product). On treatment with excess toluene followed by reduction with $NaBH_4$, the expected product, ethyltoluene (almost exclusively para), is obtained.

When *exo-cis*-3-hydroxy-2-norbornylmercuric acetate[8] (**8**) is treated with FSO_3H-SbF_5-SO_2 as described, the resulting solution cooled to −70° gives the pmr spectrum shown in Figure 2. Quenching with ice–water gives norbornylene as the only detectable organic product while quenching with $NaBH_4$-H_2O gives norbornane.

The result of the quench with $NaBH_4$ and comparison of the spectrum with that obtained by protonation of norbornylene oxide or 3-hydroxynortricyclene[9] in the same superacid solvent systems indicates that the ion **3** in Figure 1 is not a hydroxynorbornyl cation. The data are consistent only with norbornylenemercurinium ion (**3**).



3

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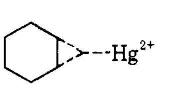
(2) There have been two recent claims of direct observation of mercurinium ions. The first, by Saito and Matsuoa,[3] was shown subsequently to be incorrect.[4] The second, by Reutov and coworkers,[5] concerns the alleged observation of mercurinium ion **1** in the system cyclo-



1

hexene–mercuric nitrate–acetonitrile–nitric acid by proton magnetic resonance spectroscopy. However, the *n* basicity of acetonitrile (used as solvent) coupled with the known reactivity of mercurinium ions toward such bases make it highly unlikely that a detectable concentration of ion **1** could exist in acetonitrile. Indeed, when ion **1** was produced in strong acid media, it was immediately quenched upon addition of acetonitrile (G. A. Olah and P. R. Clifford, to be published). Furthermore, only scanty spectral details were reported and the temperature dependence of the pmr spectrum is more consistent with an equilibrium process than with a static, discrete species such as **1**.

(3) W. Saito and M. Matsuoa, *Chem. Commun.*, 961 (1962).

(4) W. Kitching, A. J. Smith, and P. R. Wells, *ibid.*, 370 (1968).

(5) V. I. Sokolov, Yu. A. Ustynyuk, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **173**, 1103 (1967).

(6) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

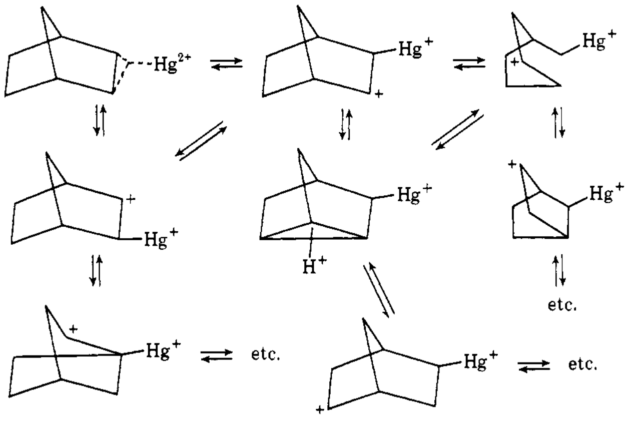
(7) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

(8) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963).

(9) (a) G. A. Olah, G. Liang, and P. R. Clifford, unpublished results; (b) protonation of norbornylene in superacids yields the well-studied norbornyl cations: G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4267 (1970).

Assignment of the pmr spectrum of ion **3** at −70° is as follows: δ 8.13 (2 H), H_2, H_3; δ 4.18 (2 H), H_1, H_4; δ 2.64 (2 H) H_5 exo, H_6 exo; δ 1.92 (1 H), H_7 syn; δ 1.49 (3 H), H_7 anti, H_5 endo, H_6 endo. Due to the complexity of the spectrum and probable peak overlap $J_{^{199}Hg-^{1}H}$ coupling in ion **3** could not be assigned. The deshieldings observed for the H_1, H_4 and H_5 exo, H_6 exo protons are analogous to the deshieldings observed for the H_1 and H_6 exo protons in the 2-methyl and 2-halonorbornyl cations.[10] The singlets at δ 3.12 and 12.30 and 13.01 are assigned to protonated acetic acid.[11] The observation that all the acetate present had been converted to protonated acetic acid, combined with the considerable deshielding of the H_2 and H_3 protons, indicates that the charge on ion **3** and by analogy on ion **2**, is 2. It is also worth noting that a ^{13}C shift of $+34.2$ ppm (relative to CS_2) for C_2 and C_3, obtained by the indor method, is entirely consistent with the proposed structure.

It is interesting to note that if a solution of ion **3** is warmed to −30° all the pmr peaks between δ 4.18 and 1.49 coalesce into a single, broad adsorption centered at ~2.7. An equilibration process such as the one shown would account for this spectral behavior. On cooling back to −70°, ion **3** is regenerated.



Our studies are being extended to the preparation and investigation of other alkylene (cycloalkylene) mercurinium ions, including their preparation *via* direct mercuration of the olefins.

Acknowledgment. Partial support of our work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowleged.

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(10) G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Amer. Chem. Soc.*, **92**, 553 (1970).

(11) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967). At −30° the dehydration of protonated acetic acid to the methyloxocarbonium ion is observed.

(12) NIH Postdoctoral Fellow, 1969–1970.

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Two New *nido*-Carborane Families: $B_7C_2H_{11}$ and $B_8C_2H_{12}$. A New Isomer of $B_5C_2H_5(CH_3)_2$[1,2]

Sir:

Several years ago we reported that volatile white crystals were formed in the reaction of acetylene with octaborane(12) in diethyl ether.[3] We now report these crystals to be *nido*-dicarbanonaborane(11) and *nido*-dicarbadecaborane(12), new members of the $B_nC_2H_{n+4}$ series of *nido*-carboranes. $B_7C_2H_{11}$ is isoelectronic with the Lewis acid B_9H_{13}, whereas $B_8C_2H_{12}$ is isoelectronic with $B_{10}H_{14}$. Numerous C-substituted $B_7C_2H_9RR'$ and $B_8C_2H_{10}RR'$ species have also been prepared.

In a typical preparation, 0.593 g of octaborane(12) (5.84 mmol) was allowed to react with 6.73 mmol of 2-butyne in a shielded trap containing 10 ml of diethyl ether. After 16 hr at 30°, the minor volatile products separated by high-vacuum fractional distillation and preparative vpc were 0.216 mmol of hydrogen, 0.400 mmol of ethane, a trace of diborane, 0.152 mmol of B_6H_{10} (2.6% yield), 0.088 mmol of the new $B_5C_2H_5(CH_3)_2$ (1.5% yield), 0.050 mmol of unreacted 2-butyne, and excess diethyl ether. The major products were separated on a low-temperature fractionation column.[4] Pure $B_7C_2H_9(CH_3)_2$ (0.255 g, 29% yield) distilled from the column between −31 and −7°, and pure $B_8C_2H_{10}(CH_3)_2$ (0.088 g, 10% yield) distilled between +3 and +11°. Repeated fractionation of the material distilling between −7 and +3° raised the yields to 58 and 20%, respectively. The overall conversion of B_8H_{12} to carboranes was 80%. Extraction and sublimation of the yellow oil remaining in the reactor trap afforded a trace of *n*-$B_{18}H_{22}$.

$B_7C_2H_9(CH_3)_2$ is an air-sensitive, clear liquid (mp −9°) of moderate thermal stability at 20°. Even using a cold inlet, the mass spectrum at 70 eV contained intense B_6C_4 and B_7C_4 and weaker B_8C_4 and B_9C_4 envelopes. At 40 eV, the B_7C_4 envelope predominated with a maximum at *m/e* 137 and a cutoff at *m/e* 140, corresponding to the $^{11}B_7{}^{12}C_4{}^{1}H_{15}{}^{+}$ ion. At 40 eV, the relative intensities were characteristic of other known *nido*-carboranes.[5] The molecular weight was determined to be 140 (calcd for $B_7C_4H_{15}$: 138.8) by freezing point depression in cyclohexane. Infrared absorption peaks at 2965 (w), 2935 (m), 2870 (w), 2575 (vs b), 2470 (w sh), 1900 (w b), 1511 (w), 1455 (m), 1444 (m sh), 1382 (m), and 1371 cm^{-1} (m) suggest the presence of B–H, B–H–B, and two $C-CH_3$ groups. Lack of absorption between 3000 and 3060 cm^{-1} and at 1320 and 1250–1280 cm^{-1} diminishes the possibilities for $\geqslant$C–H and $B-CH_3$ units, respectively.[6] The 13 weak cage vibrations observed between 710 and 1168 cm^{-1} suggest a molecule of low symmetry. Degradation in propionic acid with Pd catalyst yielded 96% *n*-butane, providing evidence that the cage carbon atoms are vicinal in $B_7C_2H_9(CH_3)_2$.

The apparent 1:1:1:2:1:1 pattern in the 70.6-MHz ^{11}B nmr spectrum (Figure 1) requires at least six magnetically nonequivalent boron environments. The 220-MHz pmr spectrum contains methyl resonances at δ −2.32 and −1.28 ppm, bridge resonances at +1.17 and +2.56 ppm, and one sharp apical quartet at 0 ppm (J = 150 cps). The remaining six cage proton resonances overlap at δ −3.02 (J ~ 150), −2.78

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(1) Studies of Boranes. XXXI. For paper XXX of this series see J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).

(2) Presented in part before the Inorganic Division at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(3) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

(4) J. Dobson and R. Schaeffer, *ibid.*, **9**, 2183 (1970).

(5) R. E. Williams in "Progress in Boron Chemistry," Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, Elmsford, N. Y., 1967, pp 81–90.

(6) R. N. Grimes, *J. Organometal. Chem.*, **8**, 45 (1967).